# Hückel Theory (tight-binding)

Alston J. Misquitta

Centre for Condensed Matter and Materials Physics
Queen Mary, University of London

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# Hückel Theory I

**Calculations without a computer**
When dealing with unsaturated conjugated systems (polyenes, acenes, graphene) we can use the Hückel approximation to allow us to perform calculations by hand (or a small computer). This method relies on the idea of $\sigma - \pi$ separability: for a planar acene, the $\pi$ orbitals (the $p_z$) are of a different symmetry from the more tightly bound $\sigma$ orbitals. The $\sigma$ orbitals are symmetric under reflection in the plane of the molecule while the $\pi$ orbitals change sign. Hence they do not mix. Consequently we can consider the $\pi$ orbitals separately from the $\sigma$. In periodic systems this method goes by the name *tight binding*.

# Hückel Theory II

We start with the linear variation equations:

$$\mathbf{Hc} = E(\mathbf{c})\mathbf{Sc}$$

and assume that our basis space is orthonormal, i.e., $\mathbf{S} = \mathbf{I}$. This gives

$$\left(\mathbf{H} - E\mathbf{I}\right)\mathbf{c} = 0.$$

This has nontrivial solutions only if

$$\det\left|\mathbf{H} - E\mathbf{I}\right| = 0$$

# Hückel Theory III

Now assume a very local form of **H**:

$$H_{ij} = \begin{cases} \alpha & \text{if } i = j \\ \beta & \text{if } i \text{ and } j \text{ neighbours} \\ 0 & \text{otherwise.} \end{cases}$$

Here $\alpha = \langle \pi_i | H | \pi_i \rangle$ can be regarded as the energy of the $\pi_i$ orbital and $\beta = \langle \pi_i | H | \pi_j \rangle$ ($i$ and $j$ are neighbouring atoms) can be regarded as a *resonance* integral coupling the two $\pi$ orbitals.

Q: How can we justify making all resonance integrals the same? You may think that there should be a dependence on the nature of the C—C bond, i.e., whether it is a single, double or triple bond. The key here is that this approximation is valid for *delocalised* systems in which all C—C bonds are equivalent.

# Hückel Theory IV

The idea here is that we solve for the energies $\epsilon_i$ and calculate the total ($\pi$) energy of the system as

$$E_{\mathrm{tot}} = \sum_i \epsilon_i .$$

Here we have used the conventional notation $\epsilon_i$ for the energies of the eigenstates.

# Hückel Theory V

**Consider ethylene**:

$\mathrm{H} - \mathrm{C} = \mathrm{C} - \mathrm{H}$

we don't care about hydrogen atoms in the Hückel approximation so this becomes:

$- \mathrm{C} = \mathrm{C} -$

It has only two carbon atoms so our basis set consists of two $2p_\pi$ atomic orbitals. Call these $\phi_1$ on carbon 1 and $\phi_2$ on carbon 2. Therefore, the eigenstates will be of the form:

$$\psi_i = c_{1i}\phi_1 + c_{2i}\phi_2.$$

Using the Hückel rules we can write the Hamiltonian matrix as:

$$H_{i,j} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

# Hückel Theory VI

The secular equation is

$$\det \begin{vmatrix} \alpha - \epsilon & \beta \\ \beta & \alpha - \epsilon \end{vmatrix} = 0$$

which leads to

$$(\alpha - \epsilon)^2 - \beta^2 = 0$$

leading to the roots:

$$\begin{aligned} \epsilon_1 &= \alpha + \beta \\ \epsilon_2 &= \alpha - \beta \end{aligned}$$

Substitute these energies in turn back into

$$(\mathbf{H} - E\mathbf{I})\,\mathbf{c} = 0.$$

# Hückel Theory VII

which takes the form

$$c_{1i}(\alpha - \epsilon_i) + c_{2i}\beta = 0$$

to get

- For $\epsilon_1$: $c_{11} = c_{12} = c$ and $\psi_1 = c(\phi_1 + \phi_2)$.
- For $\epsilon_2$: $c_{11} = -c_{12}$ and $\psi_2 = c(\phi_1 - \phi_2)$.

Since we have assumed the $\phi_i$ are orthonormal, the normalization constant $c = 1/\sqrt{2}$.

Note that since both $\alpha$ and $\beta$ are negative, $\epsilon_1 < \epsilon_2$.

We have solved our first many electron system by hand!

# Hückel Theory VIII

Now what about butadiene:

$$\text{---}\mathrm{C}{=\!=}\mathrm{C}\text{---}\mathrm{C}{=\!=}\mathrm{C}\text{---}$$

Show that the secular equation is

$$\det \begin{vmatrix} \alpha-\epsilon & \beta & 0 & 0 \\ \beta & \alpha-\epsilon & \beta & 0 \\ 0 & \beta & \alpha-\epsilon & \beta \\ 0 & 0 & \beta & \alpha-\epsilon \end{vmatrix} = 0$$

and solve for the energies and eigenfunctions.